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Scientific Report  
ALTITUDE DISTRIBUTION, ORIGIN AND FLUX  
OF SODIUM IN THE ATMOSPHERE

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#### Abstract

Taking the maximum density of Na to be 900 atoms/cc at 93 km, the equilibrium altitude distribution is calculated. It is assumed that equilibrium is first reached among the fast reactions, ionization, recombination and oxidation of Na atoms. Sodium atoms and their compounds, which are minor constituents in the atmosphere, then diffuse and a final equilibrium is reached under the joint effect of chemical equilibrium and diffusion. It is shown that the origin of Na atoms is extraterrestrial and that approximately 554 Na atoms are deposited per sq. cm. per sec in the atmosphere. The shape of the altitude distribution curve resembles fairly well with those obtained experimentally.

## 1. Introduction

Certain metallic atoms and ions have been observed in the atmosphere. Rocket-borne mass spectrometers showed the presence of  $\text{Na}^+$ ,  $\text{Mg}^+$ ,  $\text{Ca}^+$  and probably  $\text{Fe}^+$  (Istomin, 1963; Narcisi and Bailey, 1965). Again, spectroscopic studies of the night and twilight airglows have revealed the presence of Na, K, Li atoms and  $\text{Ca}^+$  ions (Sullivan and Hunten, 1964; Delannoy and Weill, 1958). The twilight airglow of Na, which is comparatively richer in the atmosphere, has been extensively studied.

The origin of sodium in the atmosphere is a subject of controversy. (Junge et al, 1962) These atoms may originate from the earthside, that is, from sea salt, volcanic or continental dusts, or from outside the earth by meteors or interplanetary or interstellar dust or material emanated from the sun.

Attempts have been made to explain the variations in the sodium resonance line intensity in the day and night airglows and also in the morning and evening twilights. Gadsden (1964) suggests that because of the oxidation of free sodium atoms during night, the effect of recombination of  $\text{Na}^+$  ions with negative  $\text{O}^-$  ions is compensated and hence there is only a slight change in the intensity of twilight Na line from the evening to the morning. There can, however, be a large seasonal variation in its intensity. According to Gadsden, the chemical reactions of Na atoms with atmospheric oxygen play an important role in the free sodium atom abundance and height distribution. Furthermore, the height distributions of all metallic atoms in the atmosphere reveal maxima in the 90-100 km altitude range (Jones, 1966), which is also the region of maximum concentration of atomic oxygen. This indicates the possibility that there exist some sort of a correlation among them.

The metallic atoms, after reacting with the atmospheric oxygen, give rise to various products. For estimating their relative abundances and height distributions, various processes which lead to equilibrium among them must be considered.

In this paper, the equilibrium concentration of Na atoms under the joint effect of various processes has been obtained. The analysis further gives the rate at which Na atoms are deposited in the atmosphere and their origin (terrestrial or extraterrestrial).

## 2. Equilibrium Processes Involving Sodium

For determining the equilibrium processes, the following chemical reactions between sodium and oxygen are considered:

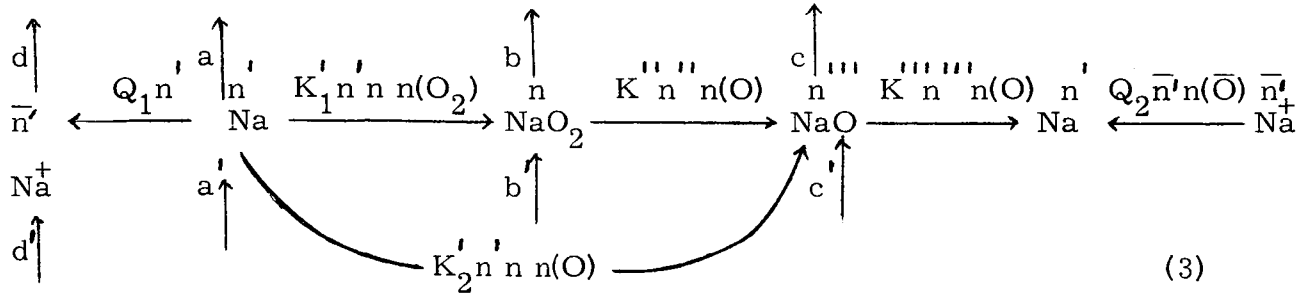


In addition, the photoionization of Na atoms and the recombination of  $\text{Na}^+$  ions with  $\text{O}^-$  ions (Bates and Boyd, 1956) should be considered, namely



where  $K_1'$ ,  $K_2'$ ,  $K''$ ,  $K'''$ ,  $Q_1$ ,  $Q_2$  are the rate coefficients of reaction.

The equilibrium concentrations of Na,  $\text{NaO}_2$ , NaO and  $\text{Na}^+$  for an average atmosphere in a layer denoted by  $n$ ,  $n'$ ,  $n''$ ,  $n'''$  and  $n^+$  respectively, are produced by the joint effect of reactions (1) and (2) and the diffusion of various sodium products. The processes which lead to the equilibrium of these constituents in any layer may be represented by the following scheme.



where  $n(\text{O}_2)$ ,  $n(\text{O})$ ,  $n(\bar{\text{O}})$ , and  $n$  are the concentrations of  $\text{O}_2$ ,  $\text{O}$ ,  $\text{O}^-$  and the total concentration in a layer of the atmosphere;  $a$  and  $a'$  are the rates at which Na atoms diffuse out and into the adjacent layers (that is,  $a'$  is the number of Na atoms which enter the given layer per second per unit area from the adjacent lower layer, and,  $a$ , those which leave the given layer to the adjacent upper layer). Similarly  $(b', b)$ ,  $(c', c)$  and  $(d', d)$  are the diffusion rates of  $\text{NaO}_2$ ,  $\text{NaO}$  and  $\text{Na}^+$  respectively.

### 3. Equilibrium Equations

Suppose that from a certain external agency (e. g. ocean or meteorites) Na atoms are continuously deposited in the atmosphere and let  $S_0$  denote the average flux or the number of atoms deposited per unit area per second in a layer. In the steady state of diffusion, the net flux of combined products of Na should be constant, that is,

$$a + b + c + d = a' + b' + c' + d' = S_0$$

$$\text{or} \quad a + b + c + d - S_0 = 0 \tag{4}$$

Assume that the direction  $z$  pointed upward is positive, then if  $S_0$  is positive, the flux is in the upward direction, that is, Na atoms originate from the earth-side. If, on the other hand,  $S_0$  is negative, the origin of these atoms is extraterrestrial. While in motion, Na atoms undergo reactions (1) and (2). All the resulting sodium products ( $\text{Na}$ ,  $\text{NaO}_2$ ,  $\text{NaO}$  and  $\text{Na}^+$ ) involve only a single Na atom and this validates Eq. (4).

If  $\omega'$ ,  $\omega''$ ,  $\omega'''$  and  $\bar{\omega}'$  be the upward vertical diffusion velocities of Na,  $\text{NaO}_2$ , NaO and  $\text{Na}^+$  at an altitude  $z$ , then

$$\begin{aligned} a &= n' \omega' \\ b &= n'' \omega'' \\ c &= n''' \omega''' \\ d &= \bar{n}' \bar{\omega}' \end{aligned}$$

Eq. (4) then becomes

$$n' \omega' + n'' \omega'' + n''' \omega''' + \bar{n}' \bar{\omega}' - S_o = 0 \quad (5)$$

The vertical diffusion velocity  $\omega$  of any minor constituent of concentration  $n$  through a stable main atmosphere at an altitude  $z$  is given by

$$\omega = -D \left[ \frac{\partial}{\partial z} (\log n) + \frac{1}{H} (\beta + \beta \alpha + \frac{m'}{m}) \right]$$

where

- $D$  - coefficient of diffusion
- $m'$  - molecular mass of the diffusing constituent
- $m$  - mean molecular mass of the main gas
- $H$  - scale height at an altitude  $z$
- $\beta$  - gradient of the scale height at  $z$
- $\alpha$  - thermal diffusion factor.

The vertical diffusion velocity  $\omega$  can be negative, zero or positive. If the constituent concentration decreases slowly with altitude, the second term in the above equation outweighs the first and the transport is in the downward direction. If, on the otherhand, the constituent concentration falls off rapidly with altitude, the first term predominates and the transport is upward. Substituting the values of  $\omega'$ ,  $\omega''$ ,  $\omega'''$  and  $\bar{\omega}'$  into Eqn. (5) we have



$$\begin{aligned}
& D' \frac{\partial n'}{\partial z} + D'' \frac{\partial n''}{\partial z} + D''' \frac{\partial n'''}{\partial z} + 2\bar{D}' \frac{\partial \bar{n}'}{\partial z} \\
& + \frac{D'n'}{H} \left( \beta + \beta \alpha' + \frac{m'}{m} \right) + \frac{D''n''}{H} \left( \beta + \beta \alpha'' + \frac{m''}{m} \right) + \frac{D'''n'''}{H} \left( \beta + \beta \alpha''' + \frac{m'''}{m} \right) \\
& + \frac{2\bar{D}'\bar{n}'}{H} \left( \beta + \beta \alpha' + \frac{\bar{m}'}{2m} \right) + S_0 = 0
\end{aligned} \tag{6}$$

In the expression for  $\bar{\omega}'$ , as  $\text{Na}^+$  — electron plasma diffuses through a neutral gas, ambipolar diffusion coefficient (which is double of the diffusion coefficient of  $\text{Na}^+$ ) is used (Ratcliffe and Weeks, 1960). Also, for the mass of  $\text{Na}^+$ , the mean molecular mass of ion-electron i.e.  $\bar{m}/2$  is used. Since below the F layer of the atmosphere, an ion suffers collisions mainly with the neutral particles, the diffusion coefficient of  $\text{Na}^+$  can be calculated using the same formula as for the neutral particles.

The continuity equation during the steady state of diffusion for all sodium products is given by

$$\frac{\partial}{\partial z} (n'\omega') + \frac{\partial}{\partial z} (n''\omega'') + \frac{\partial}{\partial z} (n'''\omega''') + \frac{\partial}{\partial z} (\bar{n}'\bar{\omega}') = 0 \tag{7}$$

Thus, in the steady state of diffusion, while the combined concentration of Na,  $\text{NaO}_2$ , NaO and  $\text{Na}^+$  remains constant with time in a layer, the concentration of an individual constituent may change. Therefore, besides the overall steady state diffusion established from layer to layer after a long period of time by the diffusion process (diffusion is slow in the 80-120 km region of the present study), local equilibrium among the various products in a layer can be established independently by rapid processes. The equilibrium concentration of the various sodium products can be obtained in any layer by considering reactions (1) and (2), so that

$$\begin{aligned}
& K_1' \cdot n' \cdot n \cdot n(\text{O}_2) + K_2' \cdot n' \cdot n \cdot n(\text{O}) + Q_1 n' = K''' n''' n(\text{O}) + Q_2 \bar{n}' n(\bar{\text{O}}) \\
& \text{and } K_1' \cdot n' \cdot n \cdot n(\text{O}_2) = K'' \cdot n'' \cdot n(\text{O})
\end{aligned}$$

Equating  $\text{Na}^+$  ion production and loss rates we have

$$Q_1 n' = Q_2 \bar{n}' n(\bar{O})$$

The concentrations of the various sodium products in any layer can, therefore, be written in terms of the concentration of Na atoms in that layer, thus

$$n'' = n' \frac{K_1' \cdot n \cdot n(O_2)}{K'' \cdot n(O)} \quad (8a)$$

$$n''' = n' \left[ \frac{K_1' \cdot n \cdot n(O_2)}{K''' \cdot n(O)} + \frac{K_2' \cdot n}{K'''} \right] \quad (8b)$$

$$\bar{n}' = n' \frac{Q_1}{Q_2 n(\bar{O})} \quad (8c)$$

Under the joint effect of chemical equilibrium and steady diffusion, the constituents Na,  $\text{NaO}_2$ , NaO and  $\text{Na}^+$  satisfy Eq. (8) and independently Eq. (6). Substituting the values of  $n''$  and  $n'''$  and  $\bar{n}'$  in terms of  $n'$  and neglecting thermal diffusion, we have from Eq. (6)

$$\begin{aligned} & \frac{\partial n'}{\partial z} \left[ D' + \left( D'' \frac{K_1'}{K''} + D''' \frac{K_1'}{K'''} \right) \frac{n n(O_2)}{n(O)} + \frac{n K_2' D'''}{K'''} + 2 \bar{D}' \frac{Q_1}{Q_2} \frac{1}{n(\bar{O})} \right] \\ & + n' \left[ \left( D'' \frac{K_1'}{K''} + D''' \frac{K_1'}{K'''} \right) \cdot \frac{\partial}{\partial z} \frac{n(O_2) \cdot n}{n(O)} + \frac{D''' K_2'}{K'''} \frac{\partial n}{\partial z} + 2 \bar{D}' \frac{Q_1}{Q_2} \frac{\partial}{\partial z} \frac{1}{n(\bar{O})} \right. \\ & + \frac{1}{mH} \left\{ D' m' + D'' m'' \frac{K_1'}{K''} \cdot \frac{n(O_2) \cdot n}{n(O)} + D''' m''' \left( \frac{K_1' n n(O_2)}{K''' \cdot n(O)} + \frac{K_2' n}{K'''} \right) + \bar{D}' \bar{m}' \frac{Q_1}{Q_2} \frac{1}{n(\bar{O})} \right\} \\ & + \frac{\beta}{H} \left\{ D' + D'' \frac{K_1' \cdot n(O_2) n}{K'' n(O)} + D''' \left( \frac{K_1' n n(O_2)}{K''' n(O)} + \frac{K_2' n}{K'''} \right) + \frac{2 \bar{D}' Q_1}{Q_2 n(\bar{O})} \right\} + S_o = 0 \end{aligned} \quad (9)$$

To eliminate the uncertainty involved in the  $O^-$  distribution, it is assumed that  $\bar{n}' = n$ . The maximum concentration of sodium,  $n'_{\max}$ , is obtained from the above equation.

$$\begin{aligned}
 n'_{\max} \left[ \left( D'' \frac{K_1'}{K''} + D''' \frac{K_1'}{K'''} \right) \frac{\partial}{\partial z} \frac{n \cdot n(O_2)}{n(O)} + D''' \frac{K_2'}{K'''} \frac{\partial n}{\partial z} \right. \\
 + \frac{1}{mH} \left\{ D' m' + D'' m'' \frac{K_1'}{K''} \frac{n(O_2)n}{n(O)} + D''' m''' \left( \frac{K_1'}{K'''} \frac{n(O_2)n}{n(O)} + \frac{K_2' n}{K'''} \right) \right. \\
 + \left. \bar{D}' \bar{m}' \right\} + \frac{\beta}{H} \left\{ D' + D'' \frac{K_1'}{K''} \frac{n(O_2)n}{n(O)} + D''' \left( \frac{K_1'}{K'''} \frac{n(O_2)n}{n(O)} + \frac{K_2' n}{K'''} \right) \right. \\
 + \left. \left. 2\bar{D}' \right\} \right] + S_o = 0. \tag{10}
 \end{aligned}$$

#### 4. Computation of $S_o$ and Altitude Distribution of Na

From the observed maximum concentration of sodium and its altitude,  $S_o$  can be determined from Eq. (10) provided other quantities are known.  $S_o$ , thus obtained, can be used in the differential Eq. (9) for computing the height distribution of Na atoms in the atmosphere. NaO and NaO<sub>2</sub> distributions can then be calculated from Na atom concentrations by using Eqns. (8a) and (8b).

At Saskatoon, the average value of  $n'_{\max}$  is about 900 atoms/cm<sup>3</sup> and occurs at an altitude of about 93 km (Sullivan and Hunten, 1964). Values of  $n$ ,  $n(O_2)$ ,  $n(O)$ ,  $m$ ,  $T$ ,  $H$ , and  $\beta$  at different altitudes are obtained at an interval of 1 km from the Cospar International Reference Atmosphere (Champion, 1965). All the atmospheric data belong to an average atmosphere. Since the value of  $n'_{\max}$  belongs to Saskatoon (52°N), all other data should belong to this latitude. In the absence of such latitudewise data, the average atmospheric data are used.

In the absence of known values of rate coefficients of reactions between sodium and oxygen, values corresponding to reactions between hydrogen and sodium are adopted as was done by Blamont and Donahue (1964). Recently Hunten (1967) has applied corrections to the rate coefficients of sodium-hydrogen reactions to give best guesses for the corresponding sodium-oxygen reactions. His values are

$$K_1' = 2 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$$

$$K_2' = 7 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$$

$$K'' \gg 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$$

$$K''' = 4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$$

Treating molecules as rigid elastic spheres, their diffusion coefficients can be calculated by the following formula

$$D = \frac{3}{8 n \sigma_{12}^2} \left[ \frac{KT(m_1 + m_2)}{2\pi m_1 m_2} \right]^{\frac{1}{2}} \quad (11)$$

where

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$$

and

$\sigma_1, \sigma_2$  — molecular diameters of the minor and main gas respectively

$K$  — Boltzmann constant

$T$  — absolute temperature

$m_1, m_2$  — masses of the two kinds of molecules

$n$  — molecular density of the main gas.

It has been shown (Golomb and MacLeod, 1966) that the values of the diffusion coefficients estimated by using the above formula are in good agreement with those measured from the radial growth of chemiluminescent trails deposited in the atmosphere. In the absence of known values of the collision diameters of atoms, molecules and ions and their structures and sizes are obtained from the knowledge of their chemical bonds and valencies. The diameter of the sphere which circumscribes their chemically determined structure has been tentatively taken to be equal to their collision diameter.

The radii of Na and  $\text{Na}^+$  are respectively 1.57Å and .95Å. The O-O bond distance in the  $\text{NaO}_2$  molecule has been reported to be  $1.28 \pm .01\text{Å}$  (Pauling, 1960). The oxygen atom ( $1s^2 2s^2 2p^4$ ) has two unpaired p-electrons which are orientated at right angles and therefore one may expect the Na-O-O angle to be nearly  $90^\circ$  (Slater, 1931) and hence the approximate shape of  $\text{NaO}_2$  molecule can be obtained by drawing two spheres ( $\text{O}^-$  molecules) each of radii 1.4Å with a distance 1.28Å between their centers, one of which is touched in a perpendicular direction by another sphere ( $\text{Na}^+$  molecule) of radius 0.95Å. Such a molecule will be circumscribed by a sphere of radius 2.54Å. Therefore, the collision diameter of  $\text{NaO}_2$  molecule may be taken equal to 5.08Å.

As all the alkali metals form some linkage, Na-O bond distance in NaO molecule may be taken equal to the sum of the radii of  $\text{Na}^+$  and  $\text{O}^-$  ions which are respectively 0.95Å and 0.81Å. The diameter of the sphere circumscribing such a molecule which may be taken as its collisional diameter, is therefore equal to 3.52Å.

Mean collisional diameters of the air molecules at different altitudes between 85 and 120 km are obtained by taking collisional diameters of  $\text{N}_2$ ,  $\text{O}_2$  and O equal to 3.15Å, 2.98Å and 1.49Å respectively.

The diffusion coefficients of Na, NaO, NaO<sub>2</sub> and Na<sup>+</sup> calculated with the help of the above values between the altitude range 85-120 km are plotted in Figure 1.

From Eq. (10), the value of  $S_0$  comes out to be  $-554 \text{ cm}^{-2} \text{ sec}^{-1}$ . Thus it is concluded that the origin of Na is extraterrestrial. The source may be meteorites, interstellar dust or solar material and approximately 554 Na atoms are deposited per sq. cm. per sec in the atmosphere. The value of  $S_0$  is however, subjected to a revision by more accurate and exact values of the atmospheric data and other constants used in the above computation. It may, however, be noted that the sign of  $S_0$  is not likely to be changed by the revised values because the positive terms in Eq. (10) are several orders smaller than the negative terms.

Using the above value of  $S_0$ , the altitude distribution of Na atoms is obtained with the help of Eq. (9) by using an IBM 7090 computer. The distribution curve (Fig. 2) resembles fairly well those obtained experimentally (Sullivan and Hunten, 1964).

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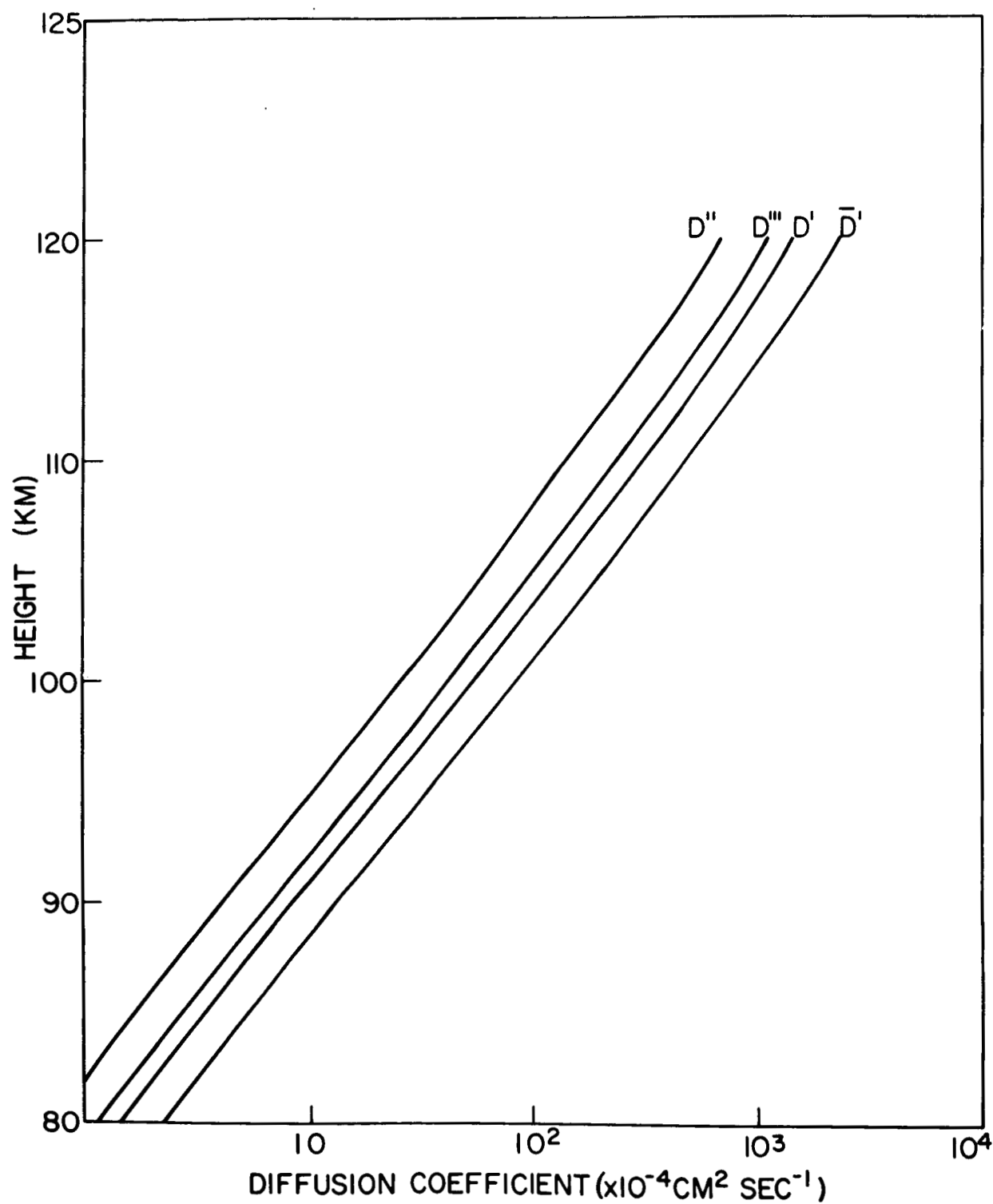


Figure Captions

Fig. 1 Calculated diffusion coefficients of Na,  $\text{Na}^+$ , NaO, and  $\text{NaO}_2$  as a function of height.

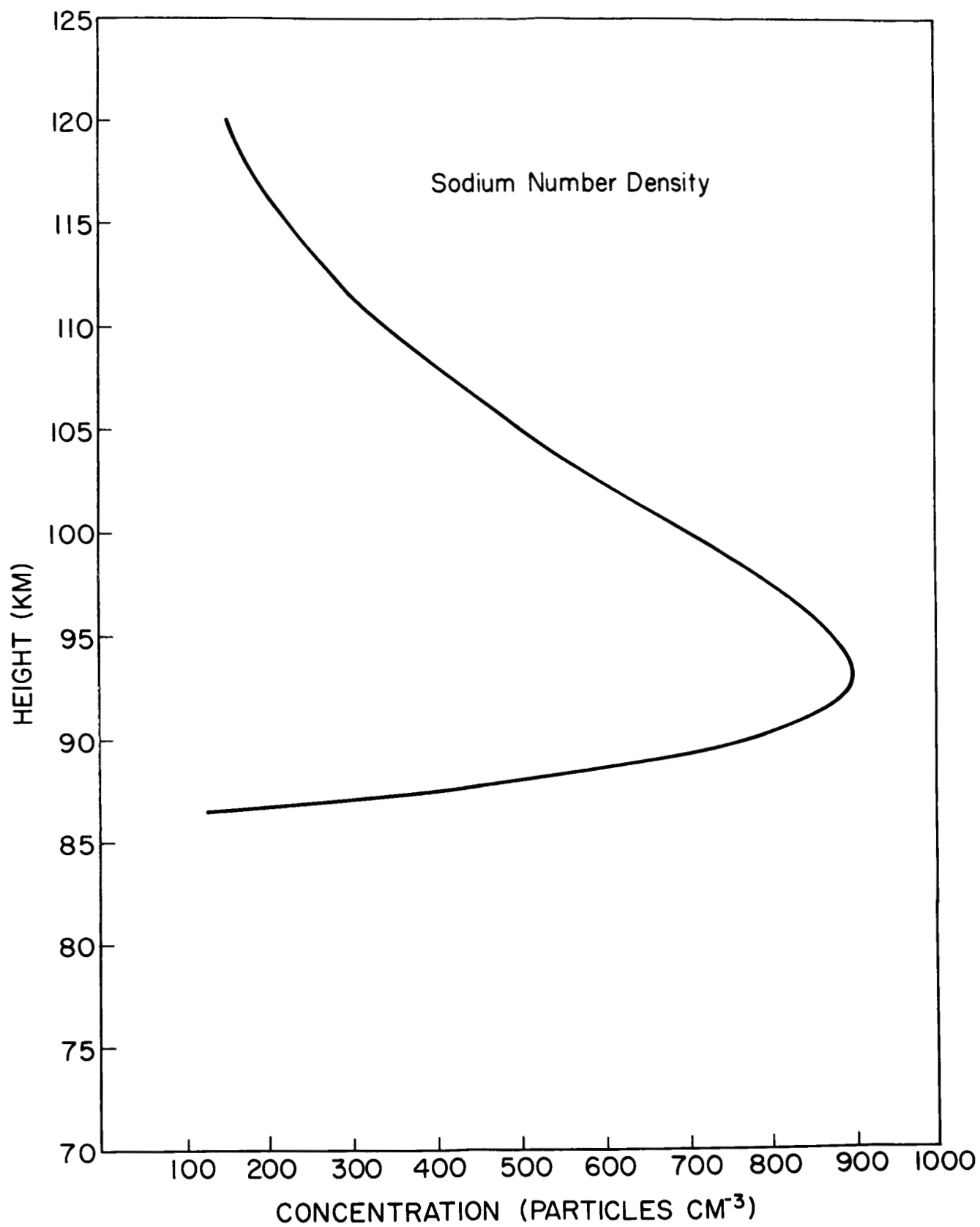


Fig. 2 The height distribution of Na atoms obtained from Eqn. (9).